

# REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-4302). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to provide information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

0128

the  
ing  
2-

1. REPORT DATE (DD-MM-YYYY) 10/01/01		2. REPORT TYPE Final Progress Report		3. DATES COVERED (From - To) 4/1/96 - 11/30/99	
4. TITLE AND SUBTITLE Processing and Characterization of Nonlinear Optical Materials				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER AFOSR F49620-96-1-0124	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Dr. Paras N. Prasad				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Research Foundation of SUNY, PO Box-9, Albany, NY-12201-0009.				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 N. RANDOLPH ST, ROOM 732 ARLINGTON VA 22203-1977				10. SPONSOR/MONITOR'S ACRONYM(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release: Distribution Unlimited				AIR FORCE SPONSOR/MONITOR'S REPORT NOTICE OF TRANSMITTAL DTIC. THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE LAW AFF 130-12. DISTRIBUTION IS UNLIMITED.	
13. SUPPLEMENTARY NOTES					

## 14. ABSTRACT

New second order ( $\chi^2$ ) materials, third order ( $\chi^3$ ) materials and photo-refractive materials were developed. A new design criterion was used to prepare a new class of  $\chi^{(2)}$  materials which would have both dipolar and octupolar contributions because of their multibranched 3 armed structures. We have developed new two-photon absorbing dyes ( $\chi^3$  materials) and their chemical conjugates for application in 3D microfabrication, 3D imaging, and optical power limiting. A major focus of our effort was careful characterization of the two-photon excited states and dynamics. For this we used femtosecond Z-scan and time-resolved pump probe experiments on the new and highly efficient multibranched fluorophore in which we discovered a new phenomenon of co-operative enhancement. We developed a two-photon fluorophores:chemotherapeutic drug conjugate and used it with two-photon laser-scanning microscopy to show the receptor-mediated entry of AN-152 into the cell cytoplasm and subsequently into the nucleus. These observations allowed a better understanding of the drug's therapeutic mechanism, which is a subject of ongoing research aimed at improving present methods for cancer therapy. Using a new approach of photosensitization with nanocrystallites of inorganic semiconductors, we have prepared photorefractive composites with good diffraction efficiency. Under this contract we have focused on developing an understanding of the basic process of photoconductivity, space charge field formation and temperature effects on kinetics in these nanocomposit

## 15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 23	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclass	b. ABSTRACT Unclass	c. THIS PAGE Unclass			19b. TELEPHONE NUMBER (include area code)

## ABSTRACT

New second order ( $\chi^2$ ) materials, third order ( $\chi^3$ ) materials and photo-refractive materials were developed. A new design criterion was used to prepare a new class of  $\chi^{(2)}$  materials which would have both dipolar and octupolar contributions because of their multibranched 3 armed structures. We have developed new two-photon absorbing dyes ( $\chi^3$  materials) and their chemical conjugates for application in 3D microfabrication, 3D imaging, and optical power limiting. A major focus of our effort was careful characterization of the two-photon excited states and dynamics. For this we used femtosecond Z-scan and time-resolved pump probe experiments on the new and highly efficient multibranched fluorophore in which we discovered a new phenomenon of co-operative enhancement. We developed a two-photon fluorophores:chemotherapeutic drug conjugate and used it with two-photon laser-scanning microscopy to show the receptor-mediated entry of AN-152 into the cell cytoplasm and subsequently into the nucleus. These observations allowed a better understanding of the drug's therapeutic mechanism, which is a subject of ongoing research aimed at improving present methods for cancer therapy. Using a new approach of photosensitization with nanocrystallites of inorganic semiconductors, we have prepared photorefractive composites with good diffraction efficiency. Under this contract we have focused on developing an understanding of the basic process of photoconductivity, space charge field formation and temperature effects on kinetics in these nanocomposit .

20010316 079

## $\chi^{(2)}$ MATERIALS

To illustrate the concept of second-harmonics by nanocrystallites the DAST-polymer nanocomposites were prepared by dispersing DAST particles (typically  $3.4 \times 10^{-3}$  M concentration) in MMA and benzoyl peroxide (1% wt) using high frequency ultrasonic processor (20 kHz). The high intensity ultrasonic waves resulted in the breaking down of the DAST crystals to submicron level. Also, the heat generated resulted in the initiation of polymerization reaction which was indicated by the increase in the viscosity of the solution. The sample was then removed and kept in the oven for complete polymerization. Due to the intrinsic noncentrosymmetric crystal structure of the nanometer particles of DAST, the DAST-polymer samples showed strong SHG signal. A green light emission was easily seen by the naked eye when the sample was pumped by 1.06  $\mu$ m Nd:YAG laser. Also, nanoparticles of other dyes (i.e. Pyrromethane 597) were dispersed in PMMA in order to achieve up-converted fluorescence.

The influence of temperature on the electro-optic properties of a polymeric composite containing the second-order nonlinear chromophore 4-(N,N-diethylamino)- $\beta$ -nitrostyrene (DEANST), was examined in the temperature range of 20 to 60°C. A modified Mach-Zehnder interferometer was used to determine the temperature dependencies of individual effective electro-optic coefficients,  $r_{13}$  and  $r_{33}$ . Also, the contributions of the birefringent-orientational effects as well as the electronic-Pockles effect to the overall electro-optic modulation measured in the composite were determined using frequency response. The dominant contribution was established to be due to birefringence. An apparent increase of electro-optic modulation with temperature and its eventual saturation was observed. This behavior is attributed to the temperature activated orientational mobility of the second-order nonlinear chromophores. A simple model based on the thermal activation of the dipolar molecule trapped in a potential well adequately explained this process. A good agreement of experimental results obtained from the direct electro-optic measurements and the indirect photorefractive investigations was achieved.

Orientational effects in the low  $T_g$  polymeric composite PVK:TCP:C<sub>60</sub>:APSS were studied both theoretically and experimentally. A theoretical derivation based on the polar order model and the rotational

diffusion equation was developed to study the enhancement of electro-optic properties of the medium by modulation of birefringence. A set of equations predicting the frequency dependence of the effective electro-optic properties as well as the frequency dependence of the phase shift between the measured light modulation and the AC voltage supplied to the sample was derived. Also, the experimental studies of the amplitude and phase of the effective electro-optic response were performed for two materials compositions with different viscomechanical properties. Our experimental results confirmed theoretically derived dependencies.

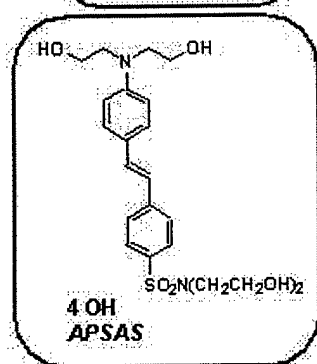
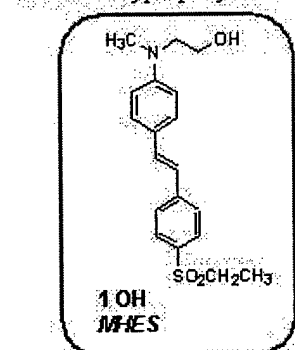
Multilayer Langmuir-Blodgett (LB) films were fabricated with two blue transparent nonlinear optical polymers in which the orientation of the nonlinear optical chromophore in one polymer is reversed with respect to the other. The intensity of the frequency-doubled light generated in these multilayers increases quadratically, with the increasing number of bilayers indicating that the macroscopic optical nonlinearity,  $\chi^{(2)}$ , of the bilayer is a linear sum of the macroscopic optical nonlinearities of the individual monolayer. Also, multilayer LB films of each blue transparent polymer were made by alternate deposition with a spacer polymer, poly(*tert*-butyl methacrylate). The intensity of the frequency-doubled light generated by these multilayer films was approximately 4 times smaller than that generated by multilayer films of two blue transparent polymers with the same number of layers, indicating that the use of another nonlinear optical active polymer in the place of passive poly(*tert*-butyl methacrylate) polymer leads to considerable improvement in the frequency-doubling efficiency. Multilayer LB films of these polymers show a great potential for achieving a practical level of performance.

We found 6-propionyl-2-dimethylaminonaphthalene (PRODAN) to be an interesting optically second order nonlinear chromophores. The molecular first hyperpolarizability,  $\beta$ , measured using the Electric Field-Induced Second Harmonic (EFISH) generation technique, was compared with that of the well known 4-nitroaniline (PNA) at fundamental wavelengths of 1064 nm and 1907 nm. The relatively large  $\beta$  value of PRODAN was shown to be thermally stable up to a treatment temperature of 200°C. The experimental measurements were complemented by semi-empirical quantum chemical calculation. Also, the value of the macroscopic second order susceptibility,  $\chi^{(2)}$ , of films produced by doping PRODAN into a

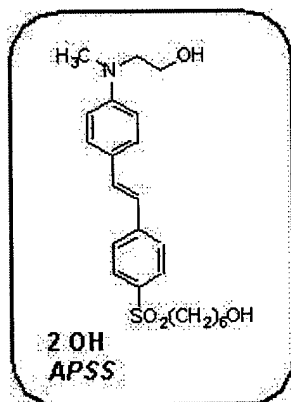
polymeric matrix and determined using the angular dependent second harmonic generation method was measured. These measurements were performed on films permanently poled under corona discharge in an *in situ* electrical poling experiment.

In  $\chi^{(2)}$  materials, our effort focused on making further modifications of the APSS type chromophore to achieve the following adjectives: (i) improved optical transparency toward the blue; (ii) produce higher thermal stability of the poled and cross-linked structure and (iii) broaden multifunctional application. Various chemical modifications made for specific applications targeted are listed below.

- Attach to main-chain
- Polyurethane (PU), Polyester (PES) etc.
- Pendant type polymer

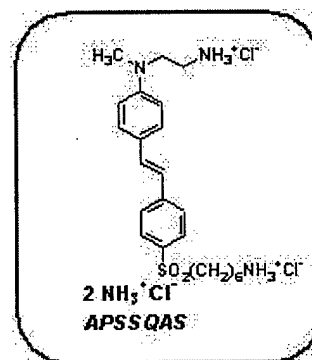
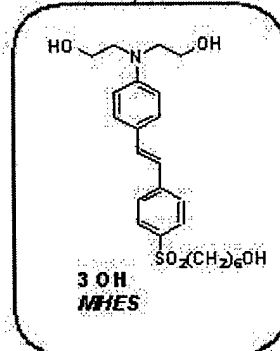


- Highly X-linked system
- Interpenetrate Network (IPN)
- Thermally stable PU



- Standard Material
- Linear Polyurethane (PU)
- X-linked w/NCO-containing liq. polymer

- X-linked PU system
- Semi-IPN
- Thermally stable PU



- Water soluble
- Confocal Microscopy

Their physical characteristics were studied. Improvement in both solubility and thermal stability was achieved. APSAS, because of having four-OH groups for cross-linking, was processed using a meta-orienting thiocyanate group. The final cross-linked and simultaneously poled structure exhibited better thermal stability of poled alignment and at the same time better transparency toward the blue.

For  $\chi^{(2)}$  materials we also developed a new design strategy to combine two-different mechanisms of nonlinearity. Traditionally, dipolar structures have been used in which a donor group is separated from an acceptor group by a conjugation unit. Recently, another group of compounds possessing a  $C_3$  symmetry have received a considerable attention as they show strong  $\chi^{(2)}$  effects derived from octupolar contributions. We have developed multibranched structures which, because of a pyramidal geometry around the N atom (of the donor group), contain both dipolar and octupolar contributions. In these structures, we found cooperative enhancement of nonlinearity.

### $\chi^{(3)}$ MATERIALS

The general behavior of two-photon-absorption enhanced refractive index change in a third-order nonlinear optical medium was studied. The nonlinear medium was the solution of a new dye, *trans*-4-[p-(N-hydroxy ethyl-N-methylamino)styryl]-N-methylpyridinium iodide (ASPI) in dimethyl sulfoxide as the solvent, which was filled into a 20-cm-long quartz hollow fiber of 100  $\mu\text{m}$  internal diameter. This dye solution has a strong two-photon absorption and subsequent upconversion fluorescence emission when excited with 1064-nm laser radiation. When the input peak intensity reached 500-1500  $\text{MW}/\text{cm}^2$  levels, obvious changes in beam profiles of the output IR laser beam were observed due to a self-focusing or self-trapping process occurring inside the fiber system. As a result of this process, highly-directional frequency-upconverted superradiant lasing output was obtained with a beam size  $\sim 5$  times smaller than that of a linearly transmitted He-Ne probe laser beam. The demonstrated mechanism can be useful for fiber laser/amplifier and fiber/integrated optics devices.

Optical limiting, pulse reshaping, and stabilization effects were achieved based on two-photon absorption mechanism via a dye-solution filled hollow fiber system. The nonlinear absorptive medium was

the solution of a new dye, *trans*-4-[p-(N-hydroxy ethyl-N-methylamino)styryl]-N-methylpyridinium iodide (ASPI) in dimethyl sulfoxide, filled into a 20 cm-long quartz hollow fiber of 100  $\mu\text{m}$  internal diameter. The input optical signal was a laser pulse train, contained  $\sim 30$  pulses of 130-ps pulsewidth. When the input peak intensity reached 400-1000  $\text{MW}/\text{cm}^2$  levels, obvious optical limiting could be observed and the envelope of the transmitted pulse train became flatter and broader. By using another new dye solution, 4-[N-(2-hydroxy ethyl)-N-(methyl)amino phenyl]-4'-(6-hydroxyhexyl sulfonyl)stilbene (APSS) in benzyl alcohol, interacting with a series of  $\sim 800$  nm laser pulses of  $\sim 8$  ns pulsewidth, a much higher nonlinear absorption coefficient and superior optical peak-power stabilization effect have been reached.

Strong two-photon absorption (TPA)-based nonlinear optical properties of a new chromophore, N,N-diphenyl-7-[2-(4-pyridinyl) ethenyl]-9,9-di-n-decyl-fluoren-2-amine (abbreviated as AF-50) was experimentally studied. This chromophore was synthesized at the Polymer Branch of the U.S. Air Force Wright Laboratory. Under excitation with 10Hz,  $\sim 8$ ns and  $\sim 800$ nm laser pulses, the TPA cross-section and TPA-induced frequency-upconverted emission spectra are measured for AF-50 solutions in various solvents. The most attractive feature of this chromophore is its remarkably high value of the molecular TPA cross-section ( $\sim 78 \times 10^{-20} \text{ cm}^2/\text{GW}$  in benzene solution). Based on this feature, superior optical power limiting and stabilization performance has been demonstrated in a 1-cm long AF-50 solution sample with a concentration of  $d_0 = 0.045 \text{ M/L}$ . The nonlinear transmission of the measured sample decreased from  $\sim 0.93$  to  $\sim 0.3$  when the input beam intensity increased from  $\sim 10 \text{ MW}/\text{cm}^2$  to  $\sim 360 \text{ MW}/\text{cm}^2$ ; the relative intensity fluctuation of the output laser pulses was reduced by two-times compared to that of the input laser beam.

Two-photon pumped upconversion intracavity lasing was achieved by placing a 1 cm-long dye-solution filled liquid cell inside a Q-switched Nd:YAG pulsed laser cavity. The upconversion gain medium is the solution of a new dye, *trans*-4-[p-(N-hydroxy ethyl-N-methylamino)styryl]-N-methylpyridinium iodide, abbreviated as ASPI, which has strong two-photon absorption and subsequent upconversion fluorescence emission when excited with the 1.06  $\mu\text{m}$  laser radiation. The spectral, temporal, and spatial properties of the upconverted cavity lasing output were investigated. The key parameters for upconversion lasing are emission wavelength of  $\sim 623 \text{ nm}$ , pulse duration of  $\sim (2-10) \text{ ns}$ , and beam

divergence of  $\sim(2.5-4)$  mrad. The corresponding parameters for the pump lasing from the same cavity are  $\sim 1.06\text{ }\mu\text{m}$ ,  $\sim 20\text{ ns}$ , and  $\sim(5-7)$  mrad, respectively. The net conversion efficiency from the absorbed IR pump laser pulse energy to the visible lasing pulse energy was measured to be  $\sim 8.5\%$ .

The two-photon absorption (TPA), TPA-induced frequency-upconversion emission, and two-photon-pumped (TPP) lasing properties of a new dye, *trans*-4-[p-(N-hydroxy ethyl-N-methylamino)styryl]-N-methylpyridinium iodide (abbreviated as ASPI) was experimentally investigated. This dye was synthesized in our Photonics Research Laboratory. This new dye has a moderate TPA cross-section ( $\sigma_2 \approx 3.9 \times 10^{-20}\text{ cm}^4/\text{GW}$  in benzyl alcohol), but exhibits a low lasing threshold and high lasing efficiency when pumped with a 1064-nm pulsed laser beam. Furthermore, the TPA-induced fluorescence yield is strongly dependent on the polarity of the solvent, making it a promising dye for sensing applications. The spectral, temporal, and spatial structures as well as the output/input characteristics of the TPP cavity lasing and the superradiant lasing are systematically measured using a 1 cm-path quartz cuvette filled with the ASPI solution or a doped polymer rod. The net conversion efficiency from the absorbed 1064-nm pump energy to the  $\sim 615\text{-nm}$  upconverted cavity lasing energy was found to be as high as  $\sim 17\%$ .

The two-photon absorption and two-photon pumped (TPP) frequency-upconverted green lasing properties of a new dye, 1-(*N*-methyl-4-pyridinio)-2-(*N*-methylpyrrol-2-yl)ethene triflate (abbreviated as M-PPE) was experimentally investigated. This dye was synthesized in the laboratory of Professor G. Pagani at University of Milan in Italy. This new dye exhibits a low lasing threshold and high lasing efficiency when pumped with a 800-nm pulsed laser beam. The spectral, temporal, and spatial structures as well as the output/input characteristics of the TPP cavity lasing were measured using a 1 cm-path quartz cuvette filled with the M-PPE solution in dimethyl sulfoxide. The net conversion efficiency from the absorbed 800-nm pump pulse energy to the  $\sim 543\text{-nm}$  upconverted cavity lasing energy was found to be as high as 11%.

Two-photon pumped (TPP) frequency-upconverted lasing properties of a partially cross-linked fluorescent polymer containing a DAST derivative was studied. This new lasing medium is a cross-linked homogeneous copolymer with two major compounds: the chromophore, 4-[bis(2-hydroxy ethyl)amino]-*N*-



methylnilbazolium iodide (DHASI), and the monomer, 2-hydroxy ethyl methacrylate (HEMA). This copolymer was synthesized in our Photonics Research Laboratory. The spectral, temporal, and spatial structures as well as the output/input characteristics of the TPP cavity lasing were measured using a 13 mm-long polymer rod. The net conversion efficiency from the absorbed 1064-nm pump pulse energy to the ~606-nm upconverted cavity lasing energy was found to be ~4%.

Optical phase-conjugation property of two-photon pumped frequency upconversion backward stimulated emission from a new dye solution was demonstrated. When the 1064 nm pump intensity reaches a certain threshold value, a highly directional and phase-conjugate backward stimulated emission at ~616 nm wavelength can be observed. After backward passing through an aberration plate placed in the input pump beam path, the introduced aberration influence (1.6-1.8 mrad) can be entirely compensated by the backward stimulated emission with a final beam divergence of 0.23 mrad only. The net conversion efficiency from the absorbed IR pump energy to the backward visible stimulated emission energy can reach 10%.

High contrast and high density three-dimensional optical data storage was demonstrated using photobleaching in a polymer block in two-photon laser scanning microscope geometry. Gray-scale in the written images was achieved by controlling the intensity of the writing beam. Both digital and analog data were written to a depth of over 100  $\mu\text{m}$  in the polymer block containing our two-photon dye, APSS, with the estimated bit dimensions being  $0.5 \times 0.5 \mu\text{m}$  laterally and 3  $\mu\text{m}$  axially. This corresponds to a storage density of the order of  $1 \times 10^{12}$  bits/ $\text{cm}^3$ . A stack of bitmap images were stored in planes one behind the other, separated by 5  $\mu\text{m}$ .<sup>14</sup> This technique was also illustrated by producing a Bugs Bunny cartoon video in which various movie frames were stored on the size of a 50  $\mu\text{m}$  spot (size of the thickness of a human hair) in different layers 5  $\mu\text{m}$  apart.

Two-photon confocal microscopy was used to obtain three dimensional images of a polymer block as well as of biological specimens. Fracture and detailed structures in the bulk at different layers up to 200  $\mu\text{m}$  deep were readily revealed. Thus 200  $\mu\text{m}$  depth limitation was due to the traveling distance limitation of the microscopic objective.

For  $\chi^{(3)}$  materials, one of our major focuses was on building a fundamental understanding of two-photon excitation dynamics. There has recently been a considerable amount of interest in two-photon processes because of their potential applications to three-dimensional optical data storage and imaging, up-conversion lasing, and optical power limiting. A major impetus to these applications has been provided by reports of molecules with a large two-photon absorption cross-section. In order to fully realize these applications, a proper understanding of the dynamics of two-photon excitation is of great importance. For example, the role of excited state absorption following a two-photon excitation with nanosecond pulses needs to be understood. The initial excitation produced by two-photon absorption may undergo relaxation in subpicoseconds and follow a complex pathway. We used experiments to probe, with ultrafast time-resolved techniques, the dynamics of two-photon excitation in two novel molecules reported to exhibit large two-photon absorption cross-sections in nanosecond experiments.

We probed the two-photon excitation dynamics of two new dyes, N,N-diphenyl-7-[2-(4-pyridinyl)ethenyl]-9,9-di-n-decyl-fluoren-2-amine (AF50) and (7-(7-benzothiazol-2-yl)-9,9-diethylfluoren-2-yl)-9,9-diethylfluoren-2-yl diphenylamine (AF250) using femtosecond excitation pulses by Z-scan and time-resolved pump-probe absorption measurements. Irradiance dependence of the induced absorption cross-section was found to be linked to linear absorption of the two-photon excited state. The excited state linear absorption cross-section are  $1.0 \cdot 10^{-17} \text{ cm}^2$  for AF250 and  $2.7 \cdot 10^{-17} \text{ cm}^2$  for AF250. Relaxation of the two-photon excited state follows a complicated path with three distinct relaxation times. The longest ones, 1.6 ns for the AF50 and 1.9 for the Af250, are associated with the respective lowest singlet lifetime: 2.23 ns and 2.15 ns.

A novel approach using an as-formed solid bulk sample containing a blend of photocurable and thermally curable epoxies together with a new highly efficient two-photon excitable fluorophore was demonstrated for in-situ fabrication of three-dimensional optical circuitry with a precise control of dimension and spacial locations. Confocal volume images of a  $1 \times 2$  splitter and a grating coupler were achieved. End-fire coupling of He-Ne laser beam into the  $1 \times 2$  splitter was also achieved.

We recently introduced a new approach where by means of energy transfer, one can couple the two mechanisms, *i.e.* two-photon absorption in one molecule with reverse saturable absorption in another molecule to produce an additional channel for enhanced power limiting. The merit of this approach is that the materials in which the two processes, *i.e.* two photon excitation and linear absorption of an incident photon from the two-photon excited state is occurring in two separate molecules which offers considerable flexibility to optimize the two processes independently. We experimentally demonstrated this approach at 800 nm by using a strong two-photon absorbing dye, AF-380, and a strong reverse saturable absorber, C<sub>60</sub>. A nanosecond time-resolved experiment was used to show that energy transfer from AF380 to C<sub>60</sub> generates triplet excitation in C<sub>60</sub> which further absorbs the pump beam to enhance the power limiting function.

In our work we used two-photon induced change in fluorescence of dyes using a pulsed IR laser beam for high-density optical data storage with storage capacity exceeding terabits per cubic centimeter. The read back was done by using either in two-photon mode using IR beam or using a CW laser like Kr/Ar laser in single-photon mode. We achieved three-dimensional storage in a polymer block doped with a new and efficient two-photon up-converting chromophore. The information was recorded in different layers at a separation of 5  $\mu\text{m}$ . Grey scale control was achieved.

Two photon laser-scanning microscopy, introduced by Webb's group, has already been shown to be a powerful technique for probing the three-dimensional structure of a cell and to have inherent optical-sectioning capability without any significant interference from autofluorescence. Our recent efforts on design and synthesis of two-photon chromophores have produced highly efficient two-photon up-converters for microscopy. We recently reported synthesis of a two-photon fluorophore, which was coupled to a chemotherapeutic agent and used in optical tracking of its interaction and entrance into the target cells by two-photon laser-scanning microscopy. Chemotherapy has been used widely in the treatment of cancers. However, the cellular mechanism of these agents is often not well understood. For example, whether certain chemotherapeutic drugs attach to the membrane of a cancer cell, enter the cell, or enter the nucleus affecting the DNA replication process is not well understood. Such an understanding at

the cellular and molecular level will be a major advancement in biology and will lead to ways of enhancing the efficacy of chemotherapy.

Chemotherapy agent AN-152 was made by coupling the cytotoxic agent doxorubicin (Dox) to the luteinizing hormone-releasing hormone (LH-RH) analog, (D-Lys<sup>6</sup>)LH-RH. Its design is based on the fact that specific high-affinity membrane receptors for LH-RH have been found to be expressed in many sex-linked tissue-derived cancers and expresses *de novo* in many other cancers. In the last decade, Nobel Laureate Schally and coworkers have developed and tested several cytotoxic LH-RH conjugates in which a wide variety of cytotoxic agents were linked to LH-RH analogs. As one of the most widely used anticancer drugs, Dox has shown to have a broad spectrum of antitumor effects. Its complex cytotoxic mechanism has been reported to involve inhibition of enzymes such as topoisomerase II, intercalation into DNA, and generation of cytotoxic radicals. By coupling an LH-RH analog with Dox, Schally and coworkers have shown that the product AN-152 has improved selectivity toward cancer cells and reduction in toxicity on normal cells. Additionally, studies *in vivo* show that AN-152 is less toxic and more potent in inhibition of tumor growth than is Dox. These tumors include prostatic, mammary, and ovarian cancers possessing LH-RH receptors. However, the cellular mechanism of action of this drug is still not well understood. Whether it acts by simply binding onto the membrane to release the cytotoxic radicals or by internalization into the cell or nucleus to interrupt the DNA replication process is of great interest. In collaboration with Schally using our two-photon fluorophore conjugated to AN-152, we have successfully traced its cellular pathway in a human breast cancer cell line expressing LH-RH receptors. The entire process of membrane association, internalization, and intracellular localization of the chemotherapeutic drug AN-152 was visualized in real time with no loss of viability of targeted cells.

The application of two-photon excited up-converted emission was also demonstrated by our group for exciting a photosensitizer photodynamic therapy drug which produces singlet oxygen to destroy the tumor. The two-photon method offers the advantage that it can be used to treat a deeper tumor.

## PHOTOREFRACTIVE MATERIALS

Temperature dependence of the photorefractive effect in a polymer composite containing poly(9-vinylcarbazole) (PVK), tricresyl phosphate (TCP), buckminsterfullerene ( $C_{60}$ ), and 4-(N,N-diethylamino)- $\beta$ -nitrostyrene (DEANST) was studied. The photoconductive, electro-optic and photorefractive properties of the material were studied in the temperature range of 22 to 61°C. An apparent increase of electro-optic modulation with temperature and its eventual saturation was observed. The polarization anisotropy between the p- and s-polarized readouts of refractive index gratings is consistent with what would be expected on the basis of directly measured effective electro-optic coefficients. By correlating the electro-optic value with the diffraction efficiency, temperature dependence of the space-charge field was obtained and explained by temperature dependencies of the dark conductivity and the photoconductivity of the material.

Temperature dependence of the steady-state diffraction was efficiently measured in DFWM configuration for the p-polarization of the reading beam. An increase in the diffracted signal with the increasing temperature of the sample is observed up to approximately 42°C, where a maximum is reached. Further temperature increase results in a lower efficiency of the grating. A similar behavior was also determined for the s-polarized readout. Significant enhancement of two-beam coupling phenomenon due to temperature was also observed in the investigated composite. Analysis of our results indicated the following conclusions explaining temperature dependence of the photorefractive effect:

- 1) thermal softening of the host matrix increases the orientational mobility of the chromophores leading to the enhanced effective electro-optic properties of the composite; this in turn allows for a deeper grating modulation. Therefore, higher diffraction efficiency is achieved,
- 2) increase of sample's temperature enhances the free charge photogeneration as well as mobility of carriers; consequently, stronger space-charge field is formed during grating recording,

- 3) temperature activated, exponential increase in dark conductivity of the polymer matrix deteriorates the ability of the composite to maintain high internal space-charge field; as a result, the diffraction efficiency decreases at higher temperatures (i.e. above 40°C).

We have succeeded in developing a new approach of thermal fixing to enhance the storage time for a holographic grating in a photorefractive polymer. A significant increase in storage time by thermal fixing of photorefractive gratings in a polymeric composite of PVK, TCP, C<sub>60</sub>, and 4-N,N-diethylamino- $\beta$ -nitrostyrene (DEANST) is demonstrated. The fixing of the volume holograms is created by quasifreezing the orientation of the linearly anisotropic chromophore molecules. The fixed photorefractive gratings can be easily erased by elevating the sample's temperature to the glass transition temperature ( $T_g$ ) of the composite. The readout of the thermally fixed first-order (1K<sub>G</sub>) grating does not require the presence of an external electric field.

The photorefractive properties of the PVK:NPP:TCP:CdS composite samples were studied by two-wave mixing and degenerate four-wave mixing techniques using an oblique experimental setup. Holographic gratings were written through the intersection of two coherent beams generated by an Ar<sup>+</sup> laser operating at 514.5 nm with s-polarization in the FWM experiment and p-polarization in the TWM experiment. The two writing beams ( $I_1$  and  $I_2$ ), intersected in the sample with incident angles of  $\theta_1 = 60^\circ$  and  $\theta_2 = 38^\circ$  (in air) respectively, creating an intensity grating with a grating spacing,  $\Lambda$ , of 1.85  $\mu\text{m}$ . In the DFWM experiment a p-polarized reading beam ( $I_r$ ) propagated in a direction opposite of one of the writing beams ( $I_1$ ). In the TWM experiments, the asymmetric energy transfer between the p-polarized writing beams was observed by monitoring the intensity of each of the writing beams by two photodetectors when an external electric field was applied. For steady state conditions, the data was collected for a period of 30 s and averaged. In the DFWM experiment the writing beams,  $I_1$  and  $I_2$ , had intensities of 218 mW/cm<sup>2</sup> and 211 mW/cm<sup>2</sup> respectively and the reading beam,  $I_r$ , had an intensity of 5.6 mW/cm<sup>2</sup>. Given this geometry, the signal counterpropagated to  $I_2$  where it was reflected by the beam splitter and detected by a photodetector. The electric field dependence of the photorefractive DFWM steady state diffraction efficiency was obtained in a sample with a thickness of 146  $\mu\text{m}$ .

Results concerning photosensitivity were presented and the Onsager formalism developed for organic systems employed in order to extract the parameters  $r_0$  and  $\Phi_0$  from the photocharge generation efficiency data. It was shown that as a sensitizing agent CdS can be more effective than  $C_{60}$  in terms of its overall ability to produce a photo-induced current. Unlike  $C_{60}$ , the electronic properties of this class of sensitizer can be tailored to suite specific applications which offers additional incentive to further explore the possibilities of these materials. We have already achieved over 8% diffraction efficiency in the blue-green region.

## PUBLICATIONS RESULTING FROM AFOSR F49620-96-1-0124 SUPPORT

1. "Synthesis, Characterization, and Second-Order Optical Nonlinearity of a Polyurethane Structure Functionalized with a Hemicyanine Dye," K.-J. Moon, H.-K. Shim, K. S. Lee, J. Zieba, and P. N. Prasad, *Macromolecules* **29**, 861-867 (1996).
2. "Efficient, Two-Photon Pumped Green Up-converted Cavity Lasing in a New Dye," J. D. Bhawalkar, G. S. He, C.-K. Park, G. Ruland, and P. N. Prasad, *Opt. Commun.* **124**, 33-37 (1996).
3. "Properties of Two-photon Pumped Cavity Lasing in Novel Dye Doped Solid Matrices," G. S. He, J. D. Bhawalkar, C.-F. Zhao, and P. N. Prasad, *IEEE J. Quantum Electronics* **32**, 749-755 (1996).
4. "Resonant Third-order Nonlinear Optical Processes in Organic Molecules," J. D. Bhawalkar, G. S. He, and P. N. Prasad, in "Photoactive Organic Materials: Sciences and Applications," Ed: F. Kajzar, Kluwer Academic Publishers, Netherlands (1996) p. 109-128.
5. "Multiphoton Resonant Nonlinear Optical Processes in Organic Molecules," P. N. Prasad and G. S. He, in "Nonlinear Optical Materials: Theory and Modeling," Eds. S. P. Karna and A. T. Yeates, ACS Symposium Series 628, ACS Publication, Washington, D.C. (1996) p. 225-236.
6. "Second Harmonic Generation in Multilayer Langmuir-Blodgett Films of Blue Transparent Organic Polymers," W. M. K. P. Wijekoon, S. K. Wijaya, J. D. Bhawalkar, P. N. Prasad, T. L. Penner, N. J. Armstrong, M. C. Ezenyilimba, and D. J. Williams, *J. Am. Chem. Soc.* **118**, 4480-4483 (1996).
7. "Sol-Gel-Derived Micron Scale Optical Fibers for Chemical Sensing," U. Narang, R. Gvishi, F. V. Bright, and P. N. Prasad, *J. Sol-Gel Sci. Tech.* **6**, 113-119 (1996).
8. "Multiphasic Nanostructured Composites: Multi-dye Tunable Solid-State Laser," G. Ruland, R. Gvishi, and P. N. Prasad, *J. Am. Chem. Soc.* **118**, 2985-2991 (1996).
9. "Structure, Spectra, and Lasing Properties of New (Aminostyryl)pyridinium Laser Dyes," C. F. Zhao, R. Gvishi, U. Narang, G. Ruland, and P. N. Prasad, *J. Phys. Chem.* **100**, 4526-4532 (1996).
10. "Characterization of a New Solvent-Sensitive Two-Photon-Induced Fluorescent (Aminostyryl)pyridinium Salt Dye," U. Narang, C. F. Zhao, J. D. Bhawalkar, F. V. Bright, and P. N. Prasad, *J. Phys. Chem.* **100**, 4521-4525 (1996).



11. "Efficient, Two-Photon Pumped Green Upconverted Cavity Lasing in a New Dye," J. D. Bhawalkar, G. S. He, C. K. Park, C. F. Zhao, G. Ruland, and P. N. Prasad, *Opt. Commun.* 124, 33-37 (1996).
12. "Multiphasic Nanostructured Composites for Photonics," P. N. Prasad, R. Gvishi, G. S. He, J. D. Bhawalkar, N. D. Kumar, G. Ruland, C. F. Zhao, and B. A. Reinhardt, *Mat. Res. Soc. Symp. Proc.* 413, 203-213 (1996).
13. "Upconversion Dye-Doped Polymer Fiber Laser," G. S. He, J. D. Bhawalkar, C. F. Zhao, C. K. Park, and P. N. Prasad, *Appl. Phys. Lett.* 68, 3549-3551 (1996).

14. "New Application for a Well-known Molecule: Prodan as an Attractive Optically-second Order Nonlinear Chromophore," J. D. Bhawalkar, J. Zieba, M. Kazmierczak, P. N. Prasad, Y. Zhang, S. Ghosal, M. K. Casstevens, and R. Burzynski, *Int. J. Nonlinear Optics* **16**, 95-107 (1996).
15. "Nonlinear Multiphoton Processes in Organic and Polymeric Materials," J. D. Bhawalkar, G. S. He, and P. N. Prasad, *Rep. Progress of Physics* **59**, 1041-1070 (1996).
16. "Two-Photon Generated Photo-Bleached Patterns in a Polymer Matrix," P. C. Cheng, J. D. Bhawalkar, S. J. Pan, J. Swiatkiewicz, J. K. Samarabandu, W. S. Liou, G. S. He, G. Ruland, N. D. Kumar, and P. N. Prasad, *Scanning* **18**, 129-131 (1996).
17. "Three-Dimensional Laser Scanning Multi-Photon Fluorescence Confocal Microscopy Using New, Efficient Upconverting Fluorophores," P. C. Cheng, S. J. Pan, J. D. Bhawalkar, J. Swiatkiewicz, J. K. Samarabandu, W. S. Liou, G. S. He, and P. N. Prasad, *Scanning* **18**, 148-149 (1996).
18. "Langmuir-Blodgett Films (Organic Polymers for Photonics Applications)," W. M. K. P. Wijekoon and P. N. Prasad, in "The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications," Ed: J. C. Salamone, CRC Press, Boca Raton, Florida, Vol. 5, p. 3552-3567 (1996).
19. "Nanostructured Materials for Photonics," N. D. Kumar, G. Ruland, M. Yoshida, M. Lal, J. Bhawalkar, G. S. He, and P. N. Prasad, *Mater. Res. Soc. Symp. Proc.* **435**, 535-546 (1996).
20. "Three-Dimensional Laser Scanning Two-Photon Fluorescence Confocal Microscopy of Polymer Materials Using a New, Efficient Upconverting Fluorophore," J. D. Bhawalkar, J. Swiatkiewicz, S. J. Pan, J. K. Samarabandu, W. S. Liou, G. S. He, R. Berezney, P. C. Cheng, and P. N. Prasad, *J. Scanning Microscopies* **18**, 562-566 (1996).
21. "New Laser Media: Dye-Doped Sol-Gel Fiber", R. Gvishi, G. Ruland, and P. N. Prasad, *Opt. Commun.* **126**, 66-72 (1996).
22. "Fabrication of Channel Waveguides from Sol-Gel-Processed Polyvinylpyrrolidone/SiO<sub>2</sub> Composite Materials", M. Yoshida and P. N. Prasad, *Appl. Opt.* **35**, 1500-1506 (1996).
23. "Multiphoton Laser Scanning Fluorescence Microscopy – From a Fluorophore and Specimen Perspective," J. D. Bhawalkar, A. Shih, S. J. Pan, W. S. Liou, J. Swiatkiewicz, B. A. Reinhardt, P. N. Prasad, and P. C. Cheng, *Journal of Bioimaging* **4**, 168-178 (1996).

24. "Novel Approaches for Three-Dimensional Optical Data Storage in Polymeric Media," P. N. Prasad, J. D. Bhawalkar, P. C. Cheng, S. J. Pan, A. Shih, N. D. Kumar, G. Ruland, and R. Burzynski, *Polym. Mater. Sci. Eng.* 75, 173-174 (1996).
25. "Third-Order Nonlinear Optical Studies of Didecyl and Didecyloxy Substituted Polyphenyls Heptamers in THF Solution and in Composite Glass by Degenerate Four-wave Mixing and Optical Kerr Gate Measurements," R. Gvishi, P. N. Prasad, B. A. Reinhardt, and A. G. Dillard, *J. Sol-Gel Sci. Technol.* 9, 157-167 (1997).
26. "Phase-Conjugate Backward Stimulated Emission from a Two-Photon Pumped Lasing Medium," G. S. He, Y. Cui, M. Yoshida, and P. N. Prasad, *Opt. Lett.* 22, 10-13 (1997).
27. "Intracavity Upconversion Lasing Within a Q-switched Nd:YAG Laser," G. S. He, Y. Cui, J. D. Bhawalkar, P. N. Prasad, and D. D. Bhawalkar, *Opt. Commun.* 133, 175-179 (1997).
28. "Excitation Dynamics in Organic Molecules, Solids, Fullerenes and Polymers," in *Proceedings of NATO Advanced Study Institute on "Spectroscopy and Dynamics of Collective Excitations in Solids,"* Ed. R. DiBartolo, Plenum Press, New York (1997) p. 203-225.
29. "Two-Photon-Resonance Enhanced Refractive Index Change and Self-Focusing in a Dye-Solution Filled Hollow Fiber System", G. S. He, M. Yoshida, J. D. Bhawalkar, and P. N. Prasad, *Appl. Opt.* 36, 1155-1163 (1997).
30. "Novel, Organically Doped, Sol-Gel Derived Materials for Photonics: Multiphasic Nanostructured Composite Monoliths and Optical Fibers," R. Gvishi, U. Narang, G. Ruland, D. N. Kumar, and P. N. Prasad, *Appl. Organomet. Chem.* 11, 107-127 (1997).
31. "Optical Limiting, Pulse Reshaping, and Stabilization with a Nonlinear Absorptive Fiber System," G. S. He, J. D. Bhawalkar, and P. N. Prasad, *Appl. Opt.* 36, 3387-3392 (1997).
32. "Multifunctional Polymers as Multi-role Materials For Photonics", *Macromol. Symp.* 118, 467-472 (1997).
33. "TiO<sub>2</sub> Nano-Particle Dispersed Polyimide Composite Optical Waveguide Materials Through Reverse Micelles," M. Yoshida, M. Lal, N. D. Kumar, and P. N. Prasad, *J. Mat. Res.* 32, 4047-4051 (1997).

34. "Photorefractivity in a Novel Polymer Composite with High Diffraction Efficiency and Broad Optical Transparency", Y. Cui, B. Swedek, K.-S. Kim and P. N. Prasad, *J. Phys. Chem.* 101, 3530-3534 (1997).
35. "Organic-Inorganic Heterojunction Light Emitting Diodes Based on Poly(p-phenylene vinylene)/Cadmium Sulfide Thin Films", N. D. Kumar, M. P. Joshi, C. S. Friend, P. N. Prasad and R. Burzynski, *Appl. Phys. Lett.* 71, 1388-1390 (1997).
36. "Nonlinear Optical Properties of a New Chromophore", G. S. He, L. Yuan, N. Cheng, J. D. Bhawalkar, P. N. Prasad, L. L. Brott, S. J. Clarson and B. A. Reinhardt, *J. Opt. Soc. Am. B* 14, 1074-1087 (1997).
37. "Studies of Two-Photon Pumped Frequency-Upconverted Lasing Properties of a New Dye Material", G. S. He, L. Yuan, Y. Cui, M. Li and P. N. Prasad, *J. Appl. Phys.* 81, 2529-2537 (1997).
38. "Nondestructive Evaluation of Polymeric Paints and Coatings Using Two-Photon Laser Scanning Confocal Microscopy", J. D. Bhawalkar, S. J. Pan, A. Shih, J. K. Samarabandu, J. Swiatkiewicz, B. A. Reinhardt, P. N. Prasad and P. C. Cheng, *Polymer Communications* 38, 4551-4555 (1997).
39. "Two-Photon Pumped Frequency-Upconversion Lasing of a New Blue-Green Dye Material", G. S. He, L. Yuan, P. N. Prasad, A. Abbotto, A. Facchetti and G. A. Pagani, *Opt. Commun.* 140, 49-52 (1997).
40. "Solid-State Tunable Cavity Lasing in a Poly(p-phenylenevinylene) Derivative Alternating Block Co-polymer", N. D. Kumar, J. D. Bhawalkar, P. N. Prasad, F. E. Karasz and B. Hu, *Appl. Phys. Lett.* 71, 999-1001 (1997).
41. "Thermal Fixing of Refractive Index Grating in a Photorefractive Polymer", N. Cheng, B. Swedek and P. N. Prasad, *Appl. Phys. Lett.* 71, 1828-1830 (1997).
42. "Two-Photon Pumped Partially Cross-Linked Polymer Laser", G. S. He, K.-S. Kim, L. Yuan, N. Cheng and P. N. Prasad, *Appl. Phys. Lett.* 71, 1619-1621 (1997).
43. "Temperature-Dependence Studies of Photorefractive Effect in a Low Glass-Transition-Temperature Polymer Composite", B. Swedek, N. Cheng, Y. Cui, J. Zieba, J. Winiarz and P. N. Prasad, *J. Appl. Phys.* 82, 5923-5931 (1997).
44. "Spectral Properties of Backward Stimulated Scattering in Liquid Carbon Disulfide", G. S. He, Y. Cui and P. N. Prasad, *JETP* 85, 850-856 (1997).

45. "Four-Wave Mixing: Applications to Fundamental Research and Photonics Technology", P. N. Prasad in Materials Characterization and Optical Probe Techniques, Eds. R. A. Lessard and H. Franke, SPIE Press, Bellingham, Washington (1997), Vol. CR 69, p. 23-42.
46. "Novel Multifunctional Polymeric Composites for Photonics", P. N. Prasad in Photonic and Optoelectronic Polymers, Eds. S. A. Jenekhe and K. J. Wynne, ACS Symposium Series 672, ACS Publication, Washington, DC (1997), p. 533-543.
47. "Two-Photon Photodynamic Therapy", J. D. Bhawalkar, N. D. Kumar, C.-F. Zhao and P. N. Prasad, J. Clinical Laser Medicine & Surgery **15**, 201-204 (1997).
48. "Enhanced Second-order Optical Non-linearity of Thiophene-spaced N-alkylpyridinium Malononitrile Zwitterions", A. Abboto, A. Facchetti, G. A. Pagani, L. Yuan and P. N. Prasad, Gazz. Chim. Ital. **127**, 165-166 (1997).
49. "The Influence of Structure and Environment on Spectroscopic and Lasing Properties of Dye-doped Glasses", R. Gvishi, G. Ruland and P. N. Prasad, Opt. Mat. **8**, 43-54 (1997).
50. "Novel Photorefractive Polymer Composites with Broad Optical Transparency and Enhanced Optical Storage Time", P. N. Prasad, B. Swedek and N. Cheng, Polym. Prepr. **38**, 512-513 (1997).
51. "A New Class of Materials for Optical Power Limiting", M. K. Casstevens, R. Burzynski, J. F. Weibel, C. Spangler, G. He and P. N. Prasad, Proc. SPIE – Int. Soc. Opt. Eng. **3146**, 152-159 (1997).
52. "Solid-State Cavity Lasing From Poly(p-phenylenevinylene)silica Nanocomposite Bulk", D. N. Kumar, J. D. Bhawalkar and P. N. Prasad, Appl. Opt. **37**, 510-512 (1998).
53. "Phase-Conjugation Properties of Two-Photon-Pumped Backward-Stimulated Emission. I. Experimental Studies", G. S. He and P. N. Prasad, J. Opt. Soc. Am. B **15**, 1078-1085 (1998).
54. "Phase-Conjugation Properties of Two-Photon Pumped Backward-Stimulated Emission. II. Theoretical Studies", G. S. He, N. Cheng, P. N. Prasad, D. Liu and S. H. Liu, J. Opt. Soc. Am. B **15**, 1086-1095 (1998).
55. "Phase-Conjugation Property of One-Photon Pumped Backward Stimulated Emission from a Lasing Medium", G. S. He and P. N. Prasad, IEEE J. Quantum Electron. **34**, 473-481 (1998).

56. "Polymerization in a Reverse Micelle Nanoreactor: Preparation of Processable Poly(p-phenylenevinylene) with Controlled Conjugation Length", M. Lal, N. D. Kumar, M. P. Joshi and P. N. Prasad, *Chem. Mat.* 10, 1065-1068 (1998).
57. "Conjugated Polymer Based Nanocomposites for Photonics Applications", P. N. Prasad, N. D. Kumar, M. Lal and M. P. Joshi, *Mat. Res. Soc. Symp. Proc.* 488, 227-236 (1998).
58. "Two-Photon Pumped Frequency-Upconversion Blue Lasing in Coumarin Dye Solution", G. S. He, R. Signorini and P. N. Prasad, *Appl. Optics* 37, 5720-5726 (1998).
59. "Highly Active Two-Photon Dyes: Design, Synthesis and Characterization Toward Application", B. A. Reinhardt, L. L. Brott, S. J. Clarkson, A. G. Dillard, J. C. Bhatt, R. Kannon, L. Yuan, G. S. He and P. N. Prasad, *Chem. Mat.* 10, 1863-1874 (1998).
60. "Inorganic-Organic Hybrid Materials for Photonics", M. Lal, M. Joshi, D. N. Kumar, C. S. Friend, J. Winiarz, T. Asefa, K. Kim and P. N. Prasad, *Mat. Res. Soc. Symp. Proc.* 519, 217-225 (1998).
61. "Multifunctional Organic-Inorganic Nanocomposites for Photonics", C. S. Friend, M. Lal, A. Biswas, J. Winiarz, L. Zhang and P. N. Prasad, *SPIE Proceedings of Symposium on "Organic-Inorganic Hybrid Materials for Photonics"*, 3469, 100-107 (1998).
62. "Optical Power Limiting and Stabilization Based on a Novel Polymer Compound", G. S. He, C. Weder, P. Smith and P. N. Prasad, *IEEE J. Quantum Electron.*, 34, 2279-2285 (1998).
63. "Energy Transfer Coupling of Two-Photon Absorption and Reverse Saturable Absorption for Enhanced Optical Power Limiting", M. K. Joshi, J. Swiatkiewicz, F. Xu, P. N. Prasad, B. A. Reinhardt and R. Kannan, *Opt. Lett.* 23, 1742-1747 (1998).
64. "Nanoscale Synthesis and Processing of Multifunctional Polymers and Composites for Photonics" N. D. Kumar, M. Lal, and P. N. Prasad in "Science and Technology of Polymers and Advanced Materials" eds. P. N. Prasad, J. E. Mark, S. H. Kandil and Z. H. Kafafi, Plenum Press (New York, 1998) p. 393-402.
65. "Longitudinally Two-Photon Pumped Leaky Waveguide Dye Film Laser", G. S. He, R. Signorini and P. N. Prasad, *IEEE J. Quantum Electron.* 34, 7-13 (1998).

66. "Two-Photon Processes: Dynamics and Applications to Photonics and Biophotonics", P. N. Prasad, M. Joshi, P. Haridas, J. Swiatkiewicz, G. S. He, J. D. Bhawalkar, K. S. Kim and B. A. Reinhardt, *Polym. Prepr.* 39, 1114-1115 (1998).
67. "Probing Two-Photon Excitation Dynamics Using Ultrafast Laser Pulses", J. Swiatkiewicz, P. N. Prasad and B. A. Reinhardt, *Opt. Commun.* 157, 135-138 (1998).
68. "Three Dimensional Optical Data Storage in a Photobleachable Dye-doped Polymer Using Two-Photon Laser Scanning Microscopy", J. D. Bhawalkar, N. D. Kumar, J. Swiatkiewicz and P. N. Prasad, *Nonlinear Optics* 19, 249-257 (1998).
69. "Dynamics of Photorefractive Grating Erasure in Polymeric Composites", Y. Cui, B. Swedek, N. Cheng, J. Zieba and P. N. Prasad, *J. Appl. Phys.* 85, 38-43 (1999).
70. "Three-Dimensional Optical Circuitry Using Two-Photon-Assisted Polymerization", M. P. Joshi, H. E. Pudavar, J. Swiatkiewicz, P. N. Prasad and B. A. Reinhardt", *Appl. Phys. Lett.* 74, 170-172 (1999).
71. "High-Density Three-Dimensional Optical Data Storage in a Stacked Compact Disk Format with Two-Photon Writing and Single Photon Readout", H. E. Pudavar, M. P. Joshi, P. N. Prasad, *Appl. Phys. Lett.* 74, 1338-1340 (1999).
72. "Observation of the Photorefractive Effect in a Hybrid Organic-Inorganic Nanocomposite", J. G. Winiarz, L. Zhang, M. Lal, C. S. Friend and P. N. Prasad, *J. Am. Chem. Soc.* 121, 5287-5295 (1999).
73. "Up-Converted Emission Observed from a Hybrid Inorganic: Organic Composite Thin Film", M. P. Joshi, R. L. DeLeon, P. N. Prasad and J. F. Garvey, *J. Appl. Phys.* 85, 3928-3930 (1999).
74. "Photogeneration, Charge Transport, and Photoconductivity of a Novel PVK/CdS-Nanocrystal Polymer Composite", J. G. Winiarz, L. Zhang, M. Lal, C. S. Friend and P. N. Prasad, *Chem. Phys.* 245, 417-428 (1999).
75. "Dye Doped Organogels: A New Medium for Two-Photon Pumped Lasing and Other Optical Applications", M. Lal, S. Pakatchi, G. S. He, K. S. Kim and P. N. Prasad, *Chem. Mat.* 11, 3012-3014 (1999).
76. "Near Field Probing of Nanoscale Nonlinear Optical Processes", D. Jakubczyk, Y. Shen, M. Lal, C. Friend, K. S. Kim, J. Swiatkiewicz and P. N. Prasad, *Opt. Lett.* 24, 1151-1153 (1999).

77. "Spontaneous Reduction of  $\text{Eu}^{3+}$  Ion in Al Co-Doped Sol-Gel Silica Matrix During Densification", A. Biswas, C. S. Friend and P. N. Prasad, *Mat. Lett.* 39, 227-231 (1999).
78. "Nanostructured Materials and Composites for Optical Power Limiting", P. N. Prasad, G. S. He, M. P. Joshi, J. Swiatkiewicz, G. Manchala, M. Lal, A. Biswas and K-S. Kim, *Nonlinear Opt.* 21, 39-47 (1999).
79. "A Chemically Labelled Cytotoxic Agent: Two-Photon Fluorophore for Optical Tracking of Cellular Pathway in Chemotherapy", X. Wang, L. J. Krebs, M. Al-Nuri, H. E. Pudavar, S. Ghosal, C. Liebow, A. A. Nagy, A. V. Schally and P. N. Prasad, *Proc. Natl. Acad. Sci.* 96, 11081-11084 (1999).
80. "Preparation and Photorefractivity in a Novel Polymer Composite with High Diffraction Efficiency and Broad Optical Transparency", K.-S. Kim, Y. Cui, B. Swedek, N. Cheng and P. N. Prasad, *Nonlinear Optics* 20, 331-345 (1999).
81. "New Frontiers of Photonics: Nanophotonics and Biophotonics", P. N. Prasad, J. Swiatkiewicz, C. Liebow, M. Lal, H. Pudavar, M. Al-Nuri, X. Wang, L. Krebs, C. S. Friend, A. Biswas, D. Jakubczyk, Y. Shen, M. Joshi, J. D. Bhawalkar and J. Winiarz, *Nonlinear Optics* 22, 289-294 (1999).
82. "Co-operative Enhancement of Two-Photon Absorption in Multi-branched Structures", S. J. Chung, K. S. Kim, T. C. Lin, G. S. He, J. Swiatkiewicz and P. N. Prasad, *J. Phys. Chem. B* 103, 10741-10745 (1999).
83. "Confocal Enhanced Optical Coherence Tomography for Nondestructive Evaluation of Paints and Coatings", F. Xu, H. Pudavar and P. N. Prasad, *Opt. Lett.* 24, 1808-1810 (1999).